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Field dependence of the dynamic properties of colloidal suspensions of $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles

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Abstract

Results of the magnetic field dependence of the complex susceptibility, of colloidal suspensions of $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles in a polarising magnetic field, H , covering the range $0\text{--}116\text{ kA m}^{-1}$ are presented. Ferromagnetic resonance is observed for both samples and from plots of the dependence of the resonant frequency f_{res} on polarising field, average values of anisotropy field, H_A , and anisotropy constant, K , are determined. In the case of the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ sample the variation in the ferromagnetic linewidth as a function of increasing polarising field shows a steady monotonic increase in contrast to that of the manganese zinc ferrite sample. This effect is attributed to the influence of the polarising field on the local canted structure. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Magnetic susceptibility; Ferrites; Resonance

1. Introduction

Previous studies on magnetic fluids by Fannin et al. using wide-band magnetic susceptibility measurements [1] have been made. Such measurements in zero and external applied magnetic fields have enabled values of internal anisotropy field, H_A , and magnetic anisotropy constant, K , to be determined [2,3]. All samples exhibited magnetic resonance. This paper describes some preliminary studies on two magnetic fluids containing NiZn ferrite particles and MnZn ferrite particles. These

samples were specifically chosen because of their different magnetic structure [4], so that an investigation of the effect of these structures on ferromagnetic resonance could be investigated.

2. Preparation and characterisation of samples

2.1. MnZn Ferrite

Aqueous solutions of manganese sulphate (1 M, i.e. 1-molar solution), zinc sulphate (1 M) and iron(III) chloride (2 M) were mixed in the appropriate quantities and added to potassium hydroxide solution (1 M) with stirring and the pH adjusted to 10. The mixture was left for 1 h at 90°C. The

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mixture was allowed to cool and oleic acid added to coat the particles. The coagulated precipitate of coated particles was washed in water, acetone and dispersed in a hydrocarbon (isopar M). The dispersion was heated to remove residual acetone which resulted in a stable colloidal suspension (magnetic fluid).

A vibrating sample magnetometer was used to measure the saturation magnetisation (at 25°C) of the fluid (0.03 T), of the uncoated particles (0.31 T), and the median particle diameter (9 nm) [5]. The particle size was also determined using TEM and Debye–Scherrer broadening of the X-ray lines. All values obtained were consistent with the magnetic measurements. Atomic absorption spectroscopy gave the elemental composition of the uncoated particles as $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$. The lattice constant of the ferrite is 0.845 ± 0.003 nm compared with the literature value of the bulk ferrite of the same composition of 0.849 nm [6]. The observed Curie (or Néel) temperature for the particles is 550 K compared to the literature value of 530 K [7].

2.2. NiZn Ferrite

The preparation of NiZn ferrite particles and their dispersion in isopar M was carried out using

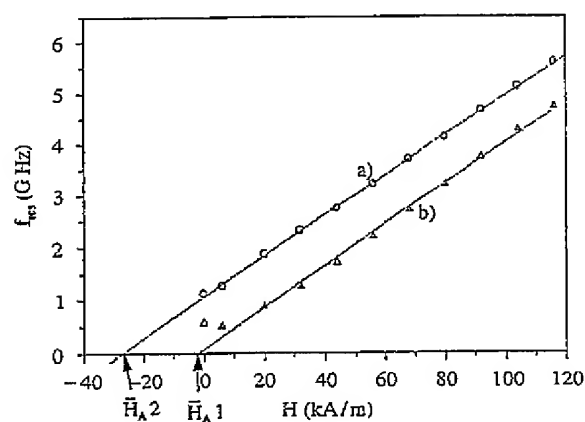


Fig. 1. (a) Plot of f_{res} against polarising field, H , for $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$, with average value of anisotropy field, $\bar{H}_A = 27 \text{ kA m}^{-1}$. (b) Plot of f_{res} against polarising field, H , for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, with average value of anisotropy field, $\bar{H}_A = 1.6 \text{ kA m}^{-1}$.

the same procedure as described for MnZn ferrite except that manganese sulphate was replaced by nickel sulphate (1 M).

Measurements of the particle diameter (9 nm) were carried out in the manner described above. The saturation magnetisation of the fluid used is 0.015 T. The elemental composition of the ferrite is $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with a lattice constant of 0.842 ± 0.003 nm compared with the literature value of the bulk value of 0.838 nm [6]. Theoretical fits of the X-ray diffraction lines for the NiZn ferrite and those for MnZn ferrite, showed no evidence of the presence of other components. The observed Curie (or Néel) temperature for the particles is 500 K compared to the literature value of 540 K [8].

3. Measurement of the complex magnetic susceptibility

Room temperature measurements of the complex magnetic susceptibility, $\chi(\omega, H) = \chi'(\omega, H) - i\chi''(\omega, H)$, of colloidal suspensions of the two ferrites described above were made using the transmission line technique [1], over the frequency range 100 MHz–6 GHz and subjected to polarising magnetic fields in the range 0–116 kA m^{-1} . Measurements were made at room temperature.

4. Results and discussion

The two samples exhibit resonance as indicated by the change in $\chi'(\omega, H)$ in passing from a positive to a negative value with increase in frequency. Plots of the resonant frequency, f_{res} , with polarising field, H , showed a linear dependence (Fig. 1), which enabled estimates of the average values of the magnetic anisotropy field, \bar{H}_A and average anisotropy constant, \bar{K} , to be determined. The field dependence of f_{res} is given by,

$$\omega_{\text{res}} = 2\pi f_{\text{res}} = \gamma(H + \bar{H}_A), \quad (1)$$

where γ is the magnetogyric ratio and has the values of $\gamma = 2.23 \times 10^5 \text{ s}^{-1} \text{ A}^{-1} \text{ m}$ and $2.47 \times 10^5 \text{ s}^{-1} \text{ A}^{-1} \text{ m}$ for the MnZn and NiZn ferrites respectively. Although ferrites have a cubic

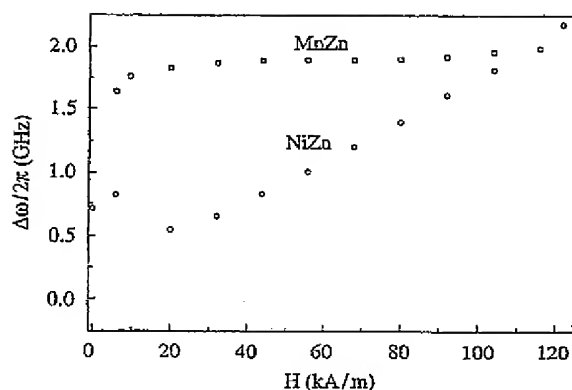


Fig. 2. (a) Plot of $\Delta\omega/2\pi$ against polarising field, H , for $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$ sample. (b) Plot of $\Delta\omega/2\pi$ against polarising field, H , for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ sample.

structure, these and other cubic ferrites studied invariably show a uniaxial anisotropy due to shape so that

$$H_A = 2\bar{K}/M_s \quad (2)$$

where M_s is the saturation magnetisation of the particulate ferrites at room temperature.

For the sample of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, $\bar{H}_A = 1.6 \text{ kA m}^{-1}$, and $\bar{K} = 180 \text{ J/m}^3$ whilst for the $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$ sample the respective values are 27 kA m^{-1} and $4 \times 10^3 \text{ J/m}^3$. The most interesting result of these preliminary investigations is the quite different behaviour of the ferromagnetic linewidth, $\Delta\omega$, (or width of the loss-peak,) as a function of polarising field as shown in Fig. 2. This figure shows that for the MnZn sample (plot (a)) the linewidth is fairly constant over the range of polarising values, whereas for the NiZn sample (plot (b)), there is a steady monotonic increase in linewidth with polarising field. A detailed review of the magnetic structures of substituted ferrites has been published by Dormann et al. [4]. It has been found that significant departures from the Néel collinear model occurs for ferrites in which non-magnetic atoms have been substituted. An excellent review on non-linear spin structures has been given by Coey [9]. These theoretical models have been used to explain these departures [10–12]. For MnZn ferrites, there is only one kind of magnetic atom in each sublattice (A and B) whereas for the

NiZn ferrites, the A site is occupied by Fe^{3+} and the B site by a mixture of the two magnetic atoms. For the composition $\text{Mn}_{0.66}\text{Zn}_{0.34}\text{Fe}_2\text{O}_4$ it has been shown that [13,14] the ferrite does not display a local canted structure or disordered magnetism whilst for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ such a structure has been observed [15,16]. It should be noted that for the samples investigated in this paper, the magnetic particles have not been annealed at high temperatures so that the spin structures may not conform exactly with the structures investigated by other workers. However, the similarities in the properties of the nano-sized particles studied here and bulk materials, gives us some confidence that the structures are not so different as to invalidate our interpretation of the data. On this assumption, the steady monotonic increase in linewidth with increasing polarising field is attributed to the effect of the local canted structure. In fact the canting angle in the B site is distributed, depending on the number of first and second next neighbours in the A site which are non magnetic. This leads to a distribution of local magnetisation values and consequently to a distribution of the local H_A values [17]. This distribution increase is expected because H perturbs the local canted states. This contributes to increased $\Delta\omega$ and thus a corresponding decrease in the maximum of the loss peak.

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